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GRAPEFRUIT CANNERY WASTE YIELDS CRUDE CITRUS PECTIN.[1]

by

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Cannery residue may be scalded, leached, pressed and dried to produce a refined pomace which may be used by jam and jelly manufacturers as a source of pectin. Most of equipment needed is available. Cost is low.

Rapid expansion of the jam and jelly industry in the United States and Allied Nations has resulted in domestic and export demands for powdered pectin in excess of the expanded capacity of the pectin industry.

Grapefruit cannery residue contains 2.5 to 4.0 percent of pectin. During the 1942-43 season, Florida canneries processed more than 17½ million boxes of grapefruit, yielding more than 322,000 tons of peel and pulp residue. Less than 60 percent of this residue was used commercially; the balance being hauled and dumped on pastures, groves and wasteland. Therefore, a large quantity of raw material for pectin is available.

The manufacture of powdered pectin requires elaborate and specialized equipment. However, the cannery residue may be scalded, leached, pressed and dried in equipment, most of which is now available, to produce a refined pomace which may be used by jam and jelly makers as a source of pectin.

Poore (1), Bosurgi and Fiedler (2), Myers and Baker (3, 4,) and others have described methods for preparing pectin from citrus fruits. All of these investigators carried the processing through to the point where they obtained a pure pectin. This report describes the production of a crude pectin or refined pomace by leaching grapefruit with water and subsequently drying and grinding the leached peel. Methods are also described for extracting the pectin from the dry pomace.

Experimental.

The basic process used in these experiments for preparing grapefruit pomace follows:

1. Grapefruit peel, obtained from a grapefruit canner, was tumbled in a wire screen (1 mesh to the inch) to remove the seeds.

2. The de-seeded peel was ground in a meat grinder, using a plate with holes ¼ in. in diameter.

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1. Agricultural Chemical Research Division Publication No. 127. Published in "Food Industries", pp. 285-287, 327-328, (April 1944).
2. Agricultural Research Administration, Bureau of Agricultural & Industrial Chem.
3. Florida Citrus Commission Research Fellows.

3. The ground material was immediately mixed with boiling water (30 gal. of water per 100 lb. of peel) and vigorously agitated for 5 minutes at a temperature ranging from 194 to 212 deg. F. By heating the peel in hot water, the pectin-destroying enzymes were inactivated (5), the peel swelled, and a large part of the water-soluble impurities were dissolved.

4. At the end of step No. 3, sufficient cool water (about 50 gal. per 100 lb. of peel) was added to lower the temperature to 135 deg. or below, and the diluted mixture further agitated for 2 minutes. The liquid was then drained off and discarded. Dilution with cool water stops any acid hydrolysis of the protopectin, tends to crisp the peel, and also dilutes the dissolved solids in the liquid.

5. The wet pomace was added to cold water (35 gal. per 100 lb. of peel), agitated for 5 minutes, and the liquid drained off and discarded.

6. Step No. 5 was repeated.

7. The leached pomace was pressed to remove all liquid possible and dried[4] until the moisture content was 4 to 8 percent. The dried material was then ground in a mill to sufficient fineness to pass through a 20-mesh screen.

An experiment was carried out to determine the effect of adding aluminum sulphate to the last leaching tank so that more of the water could be removed by pressing. Aluminum sulphate was used because it is not poisonous and any residual aluminum salt left in the pomace would not be harmful. Samples of pomace were prepared as directed above through step No. 5. The sample was then divided into two equal parts. One part was mixed with water as specified in step No. 6; the other was mixed with water to which aluminum sulphate had been added equivalent to 0.1 percent of the weight of the peel. After draining off the free liquid through a screen the two samples of pomace were pressed (400 lb. per square inch). The pressed regular pomace had a moisture content of 85.3 percent; the aluminum sulphate treated pomace had a moisture content of 77 percent. A commercial test on aluminum sulphate-treated pomace gave the results listed in Table I.

The commercial tests show that the addition of aluminum sulphate does not affect the pectin grade of the pomace and assists in removing the excess liquid.

Following the basic process and using water having a hardness of 136 parts per million (7.89 grains per U. S. gallon) as calcium carbonate, a batch of pomace was prepared and tested. It was found that 1.54 grams of pomace was required to form a standard jelly with 100 grams of sugar when extracted and treated as described later. Therefore, 1.00 gram of the pomace would gel 65 grams of sugar, and the pomace would be described as equivalent to 65-grade pectin.

Another batch was prepared by the basic process previously described, except that distilled water was used instead of tap water in step No. 3. This pomace was found equivalent to 70-grade pectin.

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4. A cabinet dryer was used in these experiments - maximum temperature, 150 deg. F.

A quantity of grapefruit pomace, using semiplant-scale equipment, was prepared for the purpose of obtaining data on the commercial production of citrus pomace. The basic process was followed, using water with a hardness of approximately 94 p.p.m. (5.45 grains per U. S. gallon) as calcium carbonate. This pomace also had a pectin grade of 70.

These three experiments indicated that water having a hardness of 136 p.p.m.(7.89 grains per U. S. gallon) or less, as calcium carbonate, may be used for leaching without materially reducing the pectin grade of the product.

In an effort to prepare a pomace containing water-soluble pectin, a quantity of peel was processed in the regular manner through step No. 5, then divided into three equal parts. One part was leached with a 2.8 percent solution of tartaric acid; another with a sulphur dioxide solution having a pH of 2.4; and the other part with a hydrochloric acid solution of pH 2.4. After leaching, the pomace was pressed and dried as usual. The dried pomace was extracted with boiling distilled water for 30 minutes. It was then cooled rapidly to room temperature and diluted to volume. The extracts were filtered clear before pectin and jelly strengths were determined. The pomace was found to be 28-grade and the amount of pectin extracted was as follows:

Acid treatment	Pectin extracted (percent)
Tartaric acid	12.03
Sulphurous acid	11.82
Hydrochloric acid	11.87

The method of extracting the pectin from the citrus pomace influences the amount and nature of the pectin extracted. The gelling power of the extract obtained is controlled by the time and temperature of extraction as well as the pH of the solution used. Vigorous agitation helps to maintain a uniform temperature of the mixture, and also keeps the pomace well dispersed throughout the solution. The apparatus designed for the purpose of securing a uniform extraction without losing water by evaporation is shown in Fig. 1. Referring to this figure, 1,000 ml. of acid solution was heated and placed in the extraction tank. After the acid solution had been brought to the desired temperature, a 20-gram sample of pomace was added, and the temperature of the mixture was maintained constant during the extraction period. In the case of sulphurous acid, the proper amount of acid was added after the water had come to the desired temperature in the extraction tank.

After extraction, the mixture was transferred to a 2-liter Erlenmeyer flask and cooled under running tap water. The cool mixture was filtered through a jelly bag using hand pressure to remove as much liquid as possible. The extract was allowed to age overnight. It was then adjusted to a pH of 3.0 $\pm$ 0.1 by neutralizing some of the acid with ammonium hyrdroxide and jelly tests were run. In the case of phosphoric acid extractions, 1 ml. of 50 percent citric acid solution was added to form a buffer salt, and then the pH was adjusted with ammonium hydroxide.

Jelly Tests for Pectin Grade*

In order to determine pectin grade, a preliminary series of jellies was prepared using varying amounts of pomace extract ranging from 1 gram to 4 grams and differing by about 0.5 gram. In each case, a weighed amount of pomace extract having a pH of 3.0 was put into a 1,000-ml. beaker and mixed with 100 grams of sugar. Distilled water was added to bring the total volume to 200 ml. and the mixture was rapidly heated, with constant stirring to prevent burning, and boiled to 65 percent sugar content (weight of mixture, 154 grams). The mixture was poured into a 4 oz. jelly glass, cooled with tap water and allowed to set overnight. The next day, the pomace jellies were compared with a standard jelly made similarly with a 100-grade pectin (1 gram of which will gel 100 grams of sugar). Finger testing was used to determine which of the test jellies agreed most closely with the standard jelly with regard to texture, resiliency and consistency. Then another series of jellies was prepared containing amounts of pomace extract, close to that used for the test jelly selected, but differing from each other by only 0.05 gram. The grade of the pectin was calculated by dividing the weight of sugar used, 100 grams, by the weight of pomace that produced a jelly which matched the standard jelly made with 100-grade pectin.

Multiple Extractions.

It was found that a second extraction of the pomace was not practicable. Five grams of pomace was extracted with 400 ml. of hydrochloric acid solution (pH 2.4) for 30 minutes at 212 deg. F. After cooling and diluting to volume, the mixture was filtered clear with the aid of Filter-Cel. The residue was extracted again with fresh acid solution and treated in the same manner as the first extract. The first and second extracts contained 0.33 gram and 0.03 gram of pectin per 100 ml., respectively.

Five grams of pomace per 100 ml. of extraction medium gave a mixture which was too thick and gummy for optimum extraction of pectin. It was decided, therefore, to use a ratio of 2 grams of pomace per 100 ml. of extraction medium.

Studies with Commercial Pomace

The results reported in this part of the work were obtained by using dried grapefruit pomace prepared on a semi-commercial scale.

It was found that a 32-mesh pomace gave a better extraction of pectin than either a 16- or 64-mesh pomace. Extractions were carried out by using a phosphoric acid solution of pH 1.5 and an extraction period of 30 minutes at a temperature of 176 deg. F. The following results were obtained:

Mesh	Pectin grade
16	70
32	77
64	50

* The grade of a pectin has been defined as the weight of sugar with which one part by weight of pectin will form a standard jelly containing 65 percent sugar solids under suitable conditions of acidity.

variables used in conjunction with each acid. Only a single extraction of the pomace was made. Twenty grams of pomace was used per 1,000 ml. of extracting medium, and all extracts were filtered through a jelly bag. The results obtained are presented in Tables II to V.

The results in Table II shows that when the pomace was treated with a citric acid solution of Ph 2.0 for 35 minutes at 208 deg. F. a pectin of 55 grade was obtained. At pH values of 2.25 and 2.5, maximum pectin grades of 35 and 30, respectively, were obtained. When the pH value of the citric acid was 2.25 and the extraction period was 60 minutes, the extracted pectin gave a pectin grade of 35. Little adjustment of the pH was necessary from the time of extraction to the finished jelly. For simplicity of procedure extraction at pH 2.0 seems to offer the greatest possibilities.

Table III shows that extraction of pectin from the pomace with sulphurous acid of pH 1.5 for 50 minutes at 176 deg. F. yielded a 45-grade pectin. Extraction with this acid of pH 2.0 for the same length of time at 208 deg. F. also yielded a 45-grade pectin. The maximum pectin grades at pH values of 2.25 and 2.50 were 38 and 30, respectively. An advantage of a sulphurous acid extraction is that the sulphur dioxide is removed during the jelly making process and thus does not leave a foreign acid in the jelly. A disadvantage is that it is necessary to buffer the extract to maintain the pH of the finished jelly at approximately 3.0.

A pectin grade of 7.0, which was the highest in these experiments, was obtained when phosphoric acid of pH 1.5 was used for a 30-minutes extraction period at 176 deg. F. (see Table IV). When using phosphoric acid solutions of pH values of 2.0, 2.25, and 2.5 the maximum pectin grades were 40, 35, and 30, respectively.

The results in Table V show that lactic acid does not appear to be a suitable extraction medium. At pH values of 2.1, 2.25, and 2.50, the maximum pectin grades obtained were 36, 35, and 25, respectively.

Table VI shows the loss of gelling power caused by filtering the pectin solution absolutely clear. The pomace was extracted with a citric acid solution and the extract obtained divided into two parts. One part was strained through a jelly bag and the other part was filtered, using a filter aid and a Buchner funnel. In each test filtration materially reduced the gelling power of the pomace extracts.

Summary and Conclusions

Methods for preparing dried citrus pomace from grapefruit peel are discussed. Enzymes may be inactivated and most of the soluble material removed by boiling the ground peel in water for 5 to 7 minutes. This treatment is followed by washing the peel with several changes of cool water. The extracted peel is then pressed to remove excess water and dried to a moisture content of 4 to 8 percent. When properly conducted, the combined washing and drying procedures result in the elimination of soluble constituents and essential oils, yielding a protopectin base of light color and neutral taste.

Laboratory and commercial tests show that the addition of aluminum sulphate to the

last leach water will change the physical character of the pomace so as to assist in removing the excess liquid by pressing without affecting the pectin grade of the finished product.

Pectin may be extracted from this raw material by means of hot acid solutions which hydrolyze the protopectin to pectin. The acid extract thus obtained can be used by manufacturers of jams, jellies and marmalades. The acidity of the organic acid solutions used, as measured by pH values, varied from 2.0 to 2.5. The inorganic acid solutions used had pH values between 1.5 and 2.5. Temperatures of extractions were 176 and 208 deg. F. Times for extraction varied from 20 minutes to 2 hours. The dried pomace which was used in these extractions was ground to pass through 16-, 32- and 64-mesh screens.

The maximum grades of the pectins extracted from the grapefruit pomace with phosphoric acid, citric acid, sulphurous acid, and lactic acid were as follows: 70, with phosphoric acid of pH 1.5 (Table IV); 55, with citric acid of pH 2.0 (Table II) 45, with sulphurous acid of pH 1.5 and 2.0 (Table III); and 36, with lactic acid of pH 2.1 (Table V).

There is some belief that the use of phosphoric acid may impart undesirable qualities to jams, jellies, and marmalades and may also create an unfavorable public reaction. Therefore, from a commercial standpoint, the citric acid extraction would probably be the most desirable. For maximum pectin yield, the use of phosphoric acid solution of pH 1.5 and an extraction period of 30 minutes at 176 deg. F. is advised. When this is objectionable, extraction of the pomace with citric acid solution at pH values from 2.0 to 2.25 for 35 to 60 minutes at 208 deg. F. is recommended.

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TABLE I -- Results of Test on Aluminum Sulphate-treated Pomace

Sample no.	Treatment	Water content of pressed material (percent)	Pectin grade of dried material
1	Water alone	90.2	50-52
2	0.1% $Al_2(SO_4)_3$	88.8	50-52
3	0.2% $Al_2(SO_4)_3$	84.6	50-52

TABLE II -- Extraction of Pomace with Citric Acid
(Temperature of Extraction, 208 deg. F.)

Citric Acid Solution		Time of extraction	pH of solution after extraction	pH of solution after adjustment	pH of finished jelly	Equivalent pectin grade
Percent strength	pH of solution	(minutes)				
1.1	2.0	35	2.70	3.05	3.03	55
1.1	2.0	50	2.50	3.04	2.97	40
1.1	2.0	70	2.47	3.02	3.05	35
0.5	2.25	40	2.77	3.07	3.05	35
0.5	2.25	60	2.82	3.00	2.99	35
0.5	2.25	80	2.81	3.05	3.03	35
0.2	2.50	60	3.81	3.01	3.00	30
0.2	2.50	80	4.12	3.00	2.98	25
0.2	2.50	120	4.51	3.03	3.01	15

TABLE III --- Extraction of Pomace with Sulphurous Acid

Sulphurous acid solution: ml. of 6% acid per liter of solution	pH of solution	Temperature of extraction deg. F.	Time of extraction (minutes)	pH of solution after extraction	pH of solution after adjustment	pH of finished jelly	Equivalent pectin grade
119	1.5	176	20	1.79	3.06	3.35	25
119	1.5	176	30	1.81	3.02	3.14	33
119	1.5	176	50	1.73	3.02	3.03	45
28	2.0	208	35	2.46	3.05	3.07	33
28	2.0	208	50	2.79	3.05	3.15	45
14.5	2.25	208	40	3.33	3.05	2.83	30
14.5	2.25	208	60	3.51	3.04	2.97	38
6.5	2.50	208	60	3.78	3.01	2.76	30
6.5	2.50	208	80	3.57	3.06	2.82	30

TABLE IV -- Extraction of Pomace with Phosphoric Acid

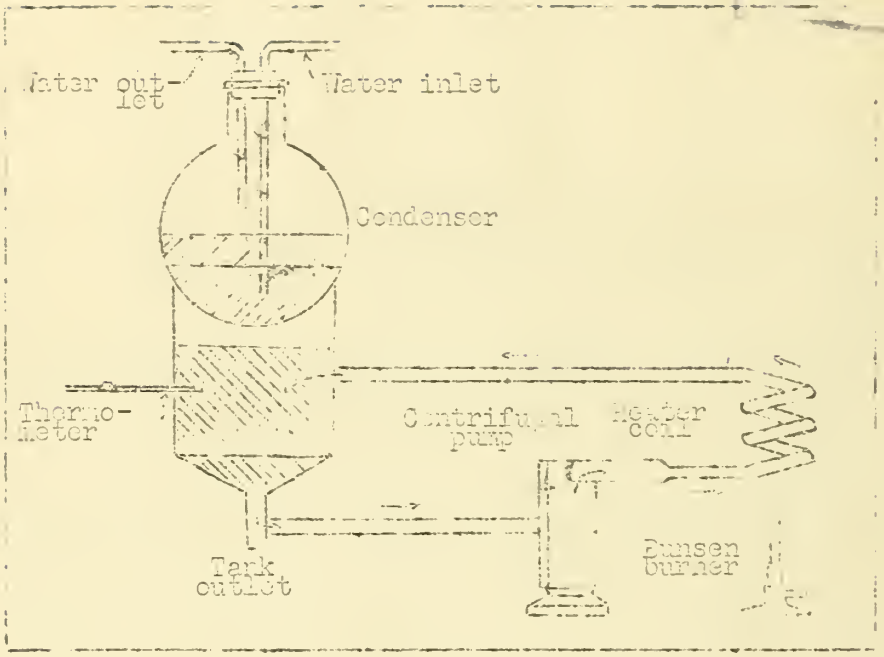
Phosphoric acid solution: ml. of 75% acid per liter of solution	pH of solution	Temperature of extraction deg. F.	Time of extraction (minutes	pH of solution after extraction	pH of solution after adjustment	pH of finished jelly	Equivalent pectin grade
7.0	1.5	176	30	1.76	3.08	3.04	70
1.7	2.0	208	35	2.75	3.02	3.08	40
1.7	2.0	208	50	2.73	3.02	3.10	35
0.8	2.25	208	40	3.28	3.03	3.05	33
0.8	2.25	208	60	3.37	3.00	3.03	35
0.3	2.50	208	60	3.67	3.02	3.04	30
0.3	2.50	208	80	3.74	3.05	3.01	25

TABLE V -- Extraction of Pomace with Lactic Acid
(Temperature of extraction, 208 deg. F)

Lactic acid solution: ml. of 50% acid per liter of solution	pH of solution	Time of extraction (minutes)	pH of solution after extraction	pH of solution after adjustment	pH of finished jelly	Equivalent pectin grade
40	2.1	35	2.58	3.03	2.97	36
40	2.1	50	2.45	3.01	3.02	33
18.75	2.25	40	2.93	3.06	2.88	33
18.75	2.25	60	2.87	3.05	2.80	35
6.0	2.50	60	3.30	3.06	2.78	25
6.0	2.50	80	3.33	3.03	2.75	25

TABLE VI -- Pomace Extract Filtered and Unfiltered
(Temperature of extraction, 208 deg. F.)

	pH of citric acid solution	Time of extraction (minutes)	pH of solution after extraction	pH of solution after adjustment	pH of finished jelly	Equivalent pectin grade
Filtered	2.0	35	2.45	3.0	3.05	45
Filtered	2.25	60	2.90	3.0	3.03	40
Unfiltered	2.0	35	2.95	2.95	3.02	65
Unfiltered	2.25	60	3.0	3.0	3.15	55



Apparatus for hydrolyzing and
extracting pectin